



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

REGION IV

345 COURTLAND STREET, N.E.  
ATLANTA, GEORGIA 30365

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Mr. John W. Walton, P.E., Director  
Division of Air Pollution Control  
Tennessee Department of Environment  
and Conservation  
L & C Annex, 9th Floor  
401 Church Street  
Nashville, Tennessee 37243-1531

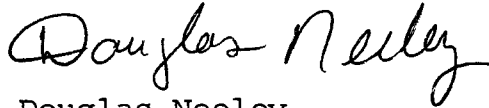
Dear Mr. Walton:

We received your letter, dated March 21, 1995, requesting guidance on EPA's "official position" regarding federal enforcement of Tennessee's ambient gaseous fluoride standard. You also asked whether this standard should be viewed as a federal requirement with respect to the title V program, once it is approved.

As stated in a letter from Mr. Douglas Neeley to you, dated March 14, 1995, the concept of federal enforceability of a SIP provision is comprised of two distinct elements. First, EPA must have a direct right under the Clean Air Act to enforce the provision at issue. Second, a provision is federally enforceable only if it is enforceable as a practical matter. EPA has not established a National Ambient Air Quality Standard (NAAQS) for fluorides or hydrogen fluoride. Although several New Source Performance Standards (NSPS) regulating total fluorides have been promulgated, these regulations were promulgated under Section 111 of the Clean Air Act specifically because fluoride is not listed as a criteria pollutant. It does not appear that the hydrogen fluoride standard bears a significant relationship to the attainment of the NAAQS. If it can be shown that there is no positive relationship between levels of hydrogen fluoride and the level of any of the criteria pollutants, then this provision would not be federally enforceable. Moreover, if this standard is not federally enforceable under title I, then it will not be federally enforceable as a title V applicable requirement.

Karen Borel in the Air Programs Branch of the Air, Pesticides and Toxics Management Division is the principal contact for this issue. If you have any questions, please contact her at (404) 347-3555, x4197.

Sincerely,

A handwritten signature in cursive script that reads "Douglas Neeley".

Douglas Neeley  
Chief  
Air Programs Branch  
Air Pesticides and Toxics  
Management Division

Air



# Primary Aluminum: Guidelines for Control of Fluoride Emissions from Existing Primary Aluminum Plants

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## 2. HEALTH AND WELFARE EFFECTS OF FLUORIDES

### 2.1 INTRODUCTION

In accordance with 40 CFR 60.22(b), promulgated on November 17, 1971 (40 FR 53340), this chapter presents a summary of the available information on the potential health and welfare effects of fluorides and the rationale for the Administrator's determination that it is a welfare-related pollutant for purposes of section 111(d) of the Clean Air Act.

The Administrator first considers potential health and welfare effects of a designated pollutant in connection with the establishment of standards of performance for new sources of that pollutant under section 111(b) of the Act. Before such standards may be established, the Administrator must find that the pollutant in question "may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare" [see section 111(b)(1)(a)]. Because this finding is, in effect, a prerequisite to the same pollutant's being identified as a designated pollutant under section 111(d), all designated pollutants will have been found to have potential adverse effects on public health, public welfare, or both.

As discussed in section 1.1 above, Subpart B of Part 60 distinguishes between designated pollutants that may cause or contribute to endangerment of public health (referred to as "health-related pollutants") and those for which adverse effects on public health have not been demonstrated ("welfare-related pollutants"). In general, the significance of the distinction is that States have more flexibility in establishing plans for the control of welfare-related pollutants than is provided for plans involving health-related pollutants.

In determining whether a designated pollutant is health-related or welfare-related for purposes of section 111(d), the Administrator considers such factors as: (1) Known and suspected effects of the pollutant on public health and welfare; (2) potential ambient concentrations of the pollutant; (3) generation of any secondary pollutants for which the designated pollutant may be a precursor; (4) any synergistic effect with other pollutants; and (5) potential effects from accumulation in the environment (e.g., soil, water and food chains).

It should be noted that the Administrator's determination whether a designated pollutant is health-related or welfare-related for purposes of section 111(d) does not affect the degree of control represented by EPA's emission guidelines. For reasons discussed in the preamble to Subpart B, EPA's emission guidelines [like standards of performance for new sources under section 111(b)] are based on the degree of control achievable with the best adequately demonstrated control systems (considering costs), rather than on direct protection of public health or welfare. This is true whether a particular designated pollutant has been found to be health-related or welfare-related. Thus, the only consequence of that finding is the degree of flexibility that will be available to the States in establishing plans for control of the pollutant, as indicated above.

## 2.2 EFFECT OF FLUORIDES ON HUMAN HEALTH<sup>1</sup>

### 2.2.1 Atmospheric Fluorides

The daily intake of fluoride inhaled from the ambient air is only a few hundredths of a milligram - a very small fraction of the total intake for the average person. If a person is exposed to ambient air containing about 8 micrograms ( $\mu\text{g}$ ) of fluoride per cubic meter, which is the maximum average concentration that is projected in the vicinity of a primary

aluminum facility with only mediocre control equipment (Table 9-5), his total daily intake from this source is calculated to be about 150  $\mu\text{g}$ . This is very low compared with the estimated daily intake of about 1200  $\mu\text{g}$  from food, water, and other sources for the average person.

Few instances of health effects in people have been attributed to community airborne fluoride, and they occurred in investigations of the health of persons living in the immediate vicinity of fluoride-emitting industries. The only effects consistently observed are decreased tooth decay and slight mottling of tooth enamel when compared to control community observations. Crippling fluorosis resulting from industrial exposure to fluoride seldom (if ever) occurs today, owing to the establishment of and adherence to threshold limits for exposure of workers to fluoride. It has never been seen in the United States. Even persons occupationally exposed to airborne fluoride do not usually come in contact with fluoride concentrations exceeding the recommended industrial threshold limit values (TLV). The current TLV for hydrogen fluoride is 3 parts per million (ppm) while that for particulate fluoride is 2.5 milligrams per cubic meter ( $\text{mg}/\text{m}^3$ ) expressed as elemental fluorine.

There is evidence that airborne fluoride concentrations that produce no plant injury contribute quantities of fluoride that are negligible in terms of possible adverse effects on human health and offer a satisfactory margin of protection for people.

Gaseous hydrogen fluoride is absorbed from the respiratory tract and through the skin. Fluoride retained in the body is found almost entirely in the bones and teeth. Under normal conditions, atmospheric

fluoride represents only a very small portion of the body fluoride burden.

### 2.2.2 Ingested Fluorides

Many careful studies, which were reviewed by the National Academy of Sciences, have been made of human populations living in the vicinity of large stationary sources of fluoride emissions. Even in situations where poisoning of grazing animals was present, no human illness due to fluoride poisoning has been found. In some of these areas much of the food used by the people was locally produced. Selection, processing and cooking of vegetables, grains and fruits gives a much lower fluoride intake in human diets than in that of animals grazing on contaminated pasture.

In poisoned animals, fluorine levels are several thousand times normal in bone, and barely twice normal in milk or meat. Calves and lambs nursing from poisoned mothers do not have fluorosis. They do not develop poisoning until they begin to graze. Meat, milk and eggs from local animals contain very little more fluoride than the same foods from unpoisoned animals. This is due to the fact that fluorine is deposited in the bones almost entirely.

### 2.3 EFFECT OF FLUORIDES ON ANIMALS<sup>1</sup>

In areas where fluoride air pollution is a problem, high-fluoride vegetation is the major source of fluoride intake by livestock. Inhalation contributes only a negligible amount to the total fluoride intake of such animals.

The available evidence indicates that dairy cattle are the domestic animals most sensitive to fluorides, and protection of dairy cattle from adverse effects will protect other classes of livestock.

Ingestion of fluoride from hay and forage causes bone lesions, lameness, and impairment of appetite that can result in decreased weight gain or diminished milk yield. It can also affect developing teeth in young animals, causing more or less severe abnormalities in permanent teeth.

Experiments have indicated that long-term ingestion of 40 ppm or more of fluoride in the ration of dairy cattle will produce a significant incidence of lameness, bone lesions, and dental fluorosis, along with an effect on growth and milk production. Continual ingestion of a ration containing less than 40 ppm will give discernible but nondamaging effects. However, full protection requires that a time limit be placed on the period during which high intakes can be tolerated.

It has been suggested that dairy cattle can tolerate the ingestion of forage that averages 40 ppm of fluoride for a year, 60 ppm for up to 2 months and 80 ppm for up to 1 month. The usual food supplements are low in fluoride and will reduce the fluoride concentration of the total ration to the extent that they are fed.

Fluoride-containing dusts can be non-injurious to vegetation but contain hazardous amounts of fluoride in terms of forage for farm animals. Phosphate rock is an example of a dust that seemingly has not injured plants but is injurious to farm animals. This was made evident forty years ago when an attempt was made to feed phosphate rock as a dietary supplement source of calcium and phosphate. Fluoride injury quickly became apparent.<sup>2</sup> Phosphate rock is used for this purpose today, but only after defluorinating by heat treatment. Phosphate rock typically contains up to about four weight percent fluorine.

## 2.4 EFFECT OF ATMOSPHERIC FLUORIDES ON VEGETATION<sup>1, 3, 4</sup>

The previous sections state that atmospheric fluorides are not a direct problem to people or animals in the United States, but that animals could be seriously harmed by ingestion of fluoride from forage. Indeed, the more important aspect of fluoride in the ambient air is its effect on vegetation and its accumulation in forage that leads to harmful effects in cattle and other animals. The hazard to these receptors is limited to particular areas: industrial sources having poorly controlled fluoride emissions and farms located in close proximity to facilities emitting fluorides.

Exposure of plants to atmospheric fluorides can result in accumulation, foliar lesions, and alteration in plant development, growth, and yield.<sup>4</sup> According to their response to fluorides, plants may be classed as sensitive, intermediate, and resistant. Sensitive plants include several conifers, several fruits and berries, and some grasses such as sweet corn and sorghum. Resistant plants include several deciduous trees and numerous vegetable and field crops. Most forage crops are tolerant or only moderately susceptible. In addition to differences among species and varieties, the duration of exposure, stage of development and rate of growth, and the environmental conditions and agricultural practices are important factors in determining the susceptibility of plants to fluorides.

The average concentration of fluoride in or on foliage that appears to be important for animals is 40 ppm. The available data suggest that a threshold for significant foliar necrosis on sensitive species, or an accumulation of fluoride in forage of more than 40 ppm would

result from exposure to a 30-day average air concentration of gaseous fluoride of about 0.5 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ).

Examples of plant fluoride exposures that relate to leaf damage and crop reduction are shown in Table 2-1.<sup>2</sup> As shown, all varieties of sorghum and the less resistant varieties of corn and tomatoes are particularly susceptible to damage by fluoride ambient air concentrations projected in the immediate vicinity of primary aluminum facilities (See Table 9-5).

## 2.5 THE EFFECT OF ATMOSPHERIC FLUORIDES ON MATERIALS OF CONSTRUCTION

### 2.5.1 Etching of Glass<sup>2</sup>

It is well known that glass and other high-silica materials are etched by exposure to volatile fluorides like HF and  $\text{SiF}_4$ . Some experiments have been performed where panes of glass were fumigated with HF in chambers. Definite etching resulted from nine hours exposure at a level of 590 ppb. Pronounced etching resulted 14.5 hours exposure at 790 ppb. Such levels would, of course, cause extensive damage to many species of vegetation. However, ambient concentrations of this magnitude are improbable provided that a aluminum facility properly maintains and operates some type of control equipment for abating fluoride emissions.

### 2.5.2 Effects of Fluorides on Structures

At the relatively low gaseous concentrations of fluorides in emissions from industrial processes, 1000 ppm or less, the damage caused by fluorides is probably limited mostly to glass and brick. Occasionally, damage to the interior brick lining of a stack has been attributed to fluorides emitted in an industrial process.

Table 2-1. EXAMPLES OF HF CONCENTRATIONS AND EXPOSURE DURATIONS REPORTED  
TO CAUSE LEAF DAMAGE AND POTENTIAL REDUCTION IN CROP VALUES<sup>2</sup>

<u>Plant</u>	<u>Concentration and time</u>	
Sorghum	0	ppb day: pb fi d
Co	pb fi	da 800 ppb fo 4 irs
to	pp fi	00 day: 00 pb fi 6 di
fi fi	00 pb	pb fi da

Fluoride damage occurs to  
for baking carbon anodes for al

rnaces

## 2.6 RATIONALE

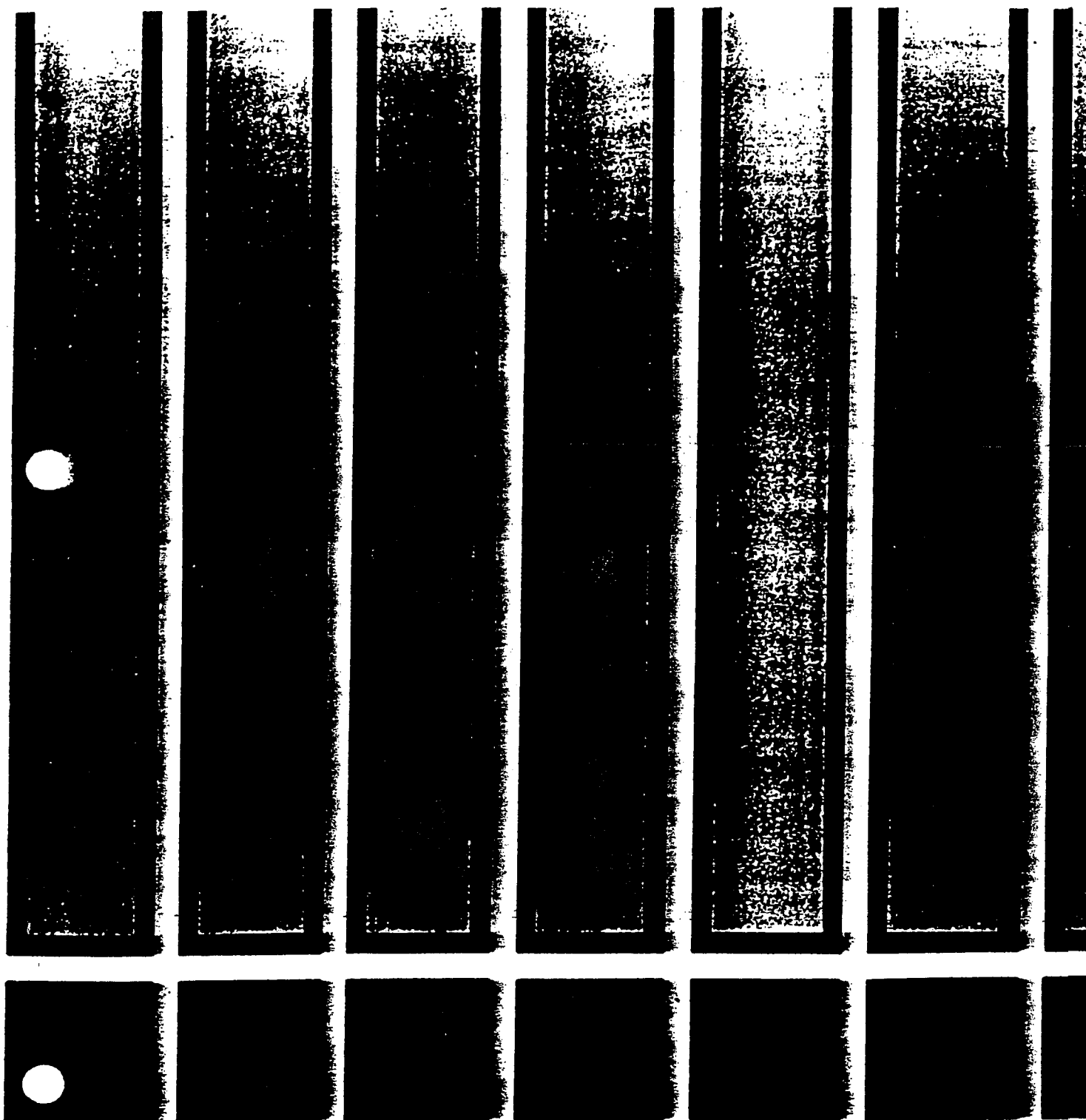
Based on the information o  
2, it is clear that fluoride em  
no significant effect on human health. Fluoride emissions, however, do  
have adverse effects on livestock and vegetation. As Table 3-3 indicates,  
most of the domestic aluminum plants are located in agricultural, dairy,  
and forest environments. Therefore the Administrator has concluded that  
fluoride emissions from primary aluminum plants do not contribute to the  
endangerment of public health. Thus, fluoride emissions will be considered  
a welfare-related pollutant for purposes of section 11(d) and Subpart B  
of Part 60.

## 2.7 REFERENCES FOR SECTION 2

1. Biologic Effects of Atmospheric Pollutants: Fluorides. National Academy of Sciences, Washington, D.C. Prepared for Environmental Protection Agency, Durham, NC, under Contract Number CPA 70-42. 1971.
2. Robinson, J. M. et al. Engineering and Cost Effectiveness Study of Fluoride Emissions Control. Resources Research, Inc. and TRW Systems Group, McLean, VA. Prepared for Office of Air Programs, Environmental Protection Agency, Durham, NC, under Contract Number EHSD 71-14. January 1972.
3. Carlson, C. E. and Dewey, J. E. Environmental Pollution by Fluorides in Flathead National Forest and Glacier National Park. U.S. Department of Agriculture - Forest Service. Missoula, Montana. October 1971.
4. Jacobson, J.S. and Hill, A.C., editors: Recognition of Air Pollution Injury to Vegetation: A Pictorial Atlas. Air Pollution Control Association and National Air Pollution Control Association, 1970. p. D1
5. Peletti, E. Corrosion and Materials of Construction. In: Phosphoric Acid, Volume I, Slack, A. V. (ed). New York, Marcel Dekker, Inc., 1978. p. 779-884.

criteria for a recommended standard  
of occupational exposure to

## HYDROGEN FLUORIDE



U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

Public Health Service      Center for Disease Control

## VII. COMPATIBILITY WITH EMISSION STANDARDS

There is presently no federal ambient air standard for hydrogen fluoride. A number of states have promulgated standards [209-213] for control of emission of fluorides. For example, Wyoming has adopted a fluoride regulation which states [209] that fluorides measured as HF in the ambient air shall not exceed  $0.80 \mu\text{g}/\text{cu m}$  or 1.0 ppb (part per billion) as a 24-hour average. Pennsylvania's standard [210] sets the limit for fluorides (total soluble as HF) as  $5 \mu\text{g}/\text{cu m}$  averaged over 24 hours. Montana's limit is 1 ppb ( $0.8 \mu\text{g}/\text{cu m}$ ) as HF. [211] Washington [212] and New York [213] set two standards, one for forage and one for ambient air. In Washington, concentration of F in forage by dry weight (calculated as F ion) is not to exceed 40 ppm averaged over 12 consecutive months, 60 ppm averaged over 2 months, and 80 ppm more than once in any 2 consecutive months. Gaseous fluorides in ambient air, calculated as HF, are not to exceed  $3.7 \mu\text{g}/\text{cu m}$ , averaged over 12 hours,  $2.9 \mu\text{g}/\text{cu m}$  for 24 hours,  $1.7 \mu\text{g}/\text{cu m}$  averaged over 7 days,  $0.84 \mu\text{g}/\text{cu m}$  averaged over 30 days, and  $0.5 \mu\text{g}/\text{cu m}$  averaged over the period March 1 through October 31 of any year. In New York, concentration of F in forage by dry weight (as F ion) is not to exceed 40 ppm averaged over a growing season not to exceed 6 months, 60 ppm averaged over 60 days, and 80 ppm averaged over any 30-day period. Gaseous fluorides, calculated as F ion, are not to exceed a 12-hour average of 4.5 ppb ( $3.7 \mu\text{g}/\text{cu m}$ ), 3.5 ppb ( $2.85 \mu\text{g}/\text{cu m}$ ) per 24-hours, 2.0 ppb ( $1.65 \mu\text{g}/\text{cu m}$ ) averaged over 1 week and 1.0 ppb ( $0.8 \mu\text{g}/\text{cu m}$ ) averaged over 1 month. The American Industrial Hygiene Association [214] recommended a Community Air Quality Guide for HF of 4.5 ppb ( $0.0036 \text{ mg}/\text{cu m}$ ) for 12

) hours, 3.5 ppb (0.0028 mg/cu m) for 24 hours, 2.0 ppb (0.0016 mg/cu m) for 1 week, and 1.0 ppb (0.0008 mg/cu m) for 1 month.

These standards were not established on the basis of protection of human health, but on the basis of damage to livestock and vegetation. levels established are well below those found to adversely affect human health.

Standards for fluorides in effluent from aluminum smelting operations have been proposed by the Environmental Protection Agency in the Federal Register 38(230):33170-83, dated 30 November 1973. The proposed 40 CFR 421 specified various concentrations of fluoride in effluent ranging from kg/1000 kg of product/day to 2.0 kg/1000 kg of product/day, depending on the process and the technology used. These limits were apparently based on biologic effects, but on the best practicable, or best available, technology.

Since these limits are not based on human health effects, they are not directly comparable with the recommended standard of Chapter I.